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IR AND THERMAL STUDIES ON BARIUM OXOMOLYBDENUM(VI) OXALATE

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ABSTRACT

The complex $Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (BMO) was prepared and characterized by chemical analysis and IR spectral studies. TG and DTA techniques were used to study the thermal decomposition. The dehydration of BMO takes place in two steps between 115 and 230°C, two moles of water being lost in each step. The decomposition of anhydrous BMO occurs between 230 and 360°C in three steps. The first two steps occur in the temperature ranges 230–255 and 255–295°C to give intermediates having the tentative compositions $Ba[Mo_2O_5(C_2O_4)(CO_3)]$ and $BaMo_2O_7\cdot CO_2$, respectively, the latter then decomposing between 295 and 360°C to give the end product. The end product consists of $BaMoO_4$, $BaMo_2O_7$ and some other phase which could not be identified.

INTRODUCTION

The technological importance of mixed oxides has attracted the attention of chemists and ceramicists to prepare them by simpler methods which have a high purity. They can be obtained by the thermal decomposition of precursor oxalates [1]. The thermal decomposition of titanyl oxalates of alkaline earths [2–4] and uranyl and plutonyl oxalates of barium [5] have been reported in the literature. Except our recent studies on the thermal decomposition of $Ba[MoO_3(C_2O_4)]\cdot 3H_2O$ [6] and $Sr[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ [7], however, no such information is available regarding the preparation and thermal decomposition of molybdenum(VI) oxalates of alkaline earths, although a molybdenum(V) oxalato complex with Ba^{2+} as the cation has been prepared and studied [8]. Hence, the present study has been undertaken to study the mode of thermal decomposition of a new molybdenum(VI) oxalato complex, $Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (BMO), which has been found to be complex and interesting. The end product is found to be a mixture of $BaMoO_4$, $BaMo_2O_7$ and some other phase which could not be identified.

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EXPERIMENTAL

All the reagents used were either of AnalaR or Proanalysi grade. To a hot solution of 1.2605 g of oxalic acid in about 200 ml of doubly distilled water, 1.4396 g of MoO_3 (prepared by heating ammonium paramolybdate at about 400°C for 2 h) were added in small lots. The solution was filtered to remove any unreacted MoO_3 and 1.2214 g of barium chloride were then added. The solution was concentrated to about 35 ml and allowed to stand overnight, to obtain crystals of BMO which were washed with water and dried in a vacuum desiccator.

Barium and molybdenum in BMO were determined gravimetrically as barium sulphate and molybdenyl oxinate, respectively, and oxalate was determined by permanganate oxidation. The results of the chemical analysis of BMO are: Ba^{2+}, 20.85; Mo, 29.20; $C_2O_4^{2-}$, 26.75% and the calculated values for $Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ are: Ba^{2+}, 20.89; Mo, 29.19; $C_2O_4^{2-}$, 26.77%. These data confirm the composition of BMO to be $Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Stanton-Redcroft TG 770 thermobalance and a DTA 673-4, respectively. Samples of 5–10 mg were used for TG and the heating rate was 3°C min^{-1}. For DTA, about 20-mg samples were used and the heating rate

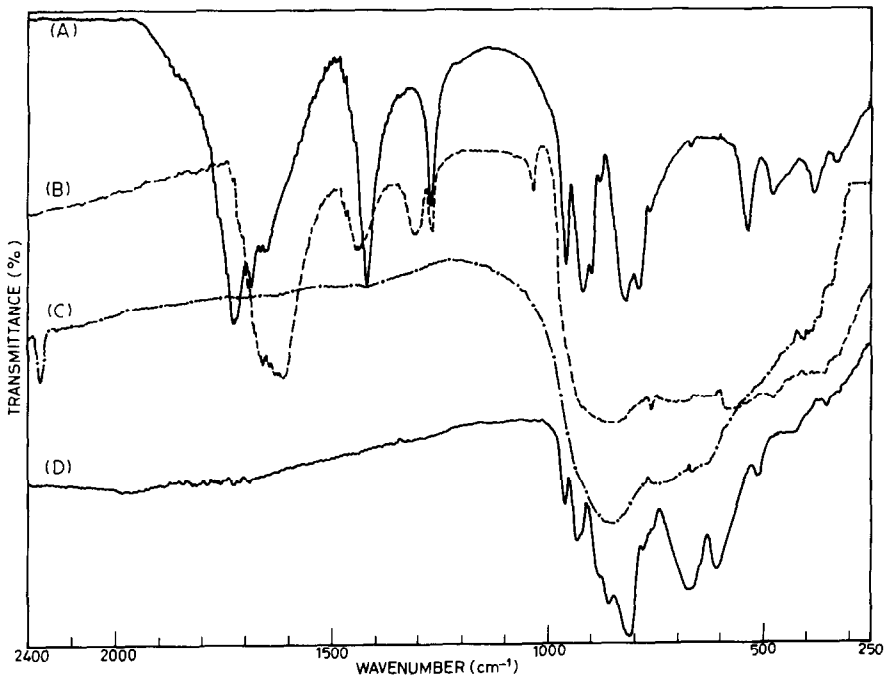

Fig. 1. IR spectra of BMO (A), BMO heated to 255°C (B); 295°C (C); and 370°C (D).

was 10°C min^{-1}. Both studies were carried out in an atmosphere of static air. IR spectra were recorded in KBr matrix on a Beckman IR-20 double-beam instrument in the range 250–4000 cm^{-1}. The X-ray diffraction patterns were taken on a Philips diffractometer using Cu$K\alpha$ radiation. They reveal that BMO is a crystalline compound of a low symmetry class. The magnetic measurements were made on a Vibrating Sample Magnetometer (model VSM-155) at room temperature (23°C), using a magnetic field of 5500 Gauss.

RESULTS AND DISCUSSION

BMO is a white crystalline compound and is found to be diamagnetic in nature suggesting that it is a molybdenum(VI) complex. The results of the IR studies of BMO (Fig. 1A) are summarized in Table 1. In addition to the bands due to the coordinated oxalato group, which have been assigned on the basis of existing data in the literature [9,10], BMO shows three strong

TABLE 1

IR data on BMO and *d* spacings for the new phase P

IR data		X-ray data, *d* spacings, $\lambda = 1.5405$ Å	
Band position (cm^{-1})	Probable assignment		
3500 S, br	ν(OH)	6.6513 [a]	1.8107 [d]
1720			
1680 VS	ν_{as}(C=O)	4.4302 [c]	1.7769 [d]
1660			
1420 S	ν_s(C–O) + ν(C–C)	4.3130 [c]	1.7562 [d]
1270 S	ν_s(C–O) + δ(O–C=O)	3.8306 [d]	1.7369 [d]
960 S	ν_{as}Mo=O	3.6302 [c]	1.7179 [d]
920 S	ν_sMo=O	3.3297 [a]	1.6966 [c]
900 W	Coordinated water	2.9074 [c]	1.6751 [d]
880 W	ν_s(C–O) + δ(O–C=O)	2.7402 [d]	1.5324 [d]
820 S	δ(O–C=O) + ν(M–O)	2.2947 [d]	1.5238 [d]
785 S	ν(O–Mo–O)	2.1287 [d]	1.4783 [d]
765 W	Coordinated water	1.8900 [d]	1.4409 [d]
670 W	Coordinated water	1.8726 [c]	1.3864 [d]
540 M	ν(M–O) + ν(C–C)		
480 M	Ring def. + δ(O–C=O)		
380 M	δ(O–C=O)		

VS = very strong, S = strong, M = medium, W = weak, br = broad; s = symmetric, as = asymmetric, δ = bending.

[a] Strongest.

[b] Very strong.

[c] Strong.

[d] Weak.

bands at 960, 920 and 785 cm^{-1}. The first two bands suggest the presence of metal–oxygen double bonds while the band at 785 cm^{-1} probably results from an O–Mo–O stretch [11,12]. In addition to these, three weak bands at 900, 765 and 670 cm^{-1} have also been observed which are probably due to the rocking, wagging and the metal–oxygen stretching vibrations, respectively, of the coordinated water [13].

Figure 2 gives the TG, DTA and differential thermogravimetric (DTG) curves of BMO in an atmosphere of static air. BMO loses its water in two steps, which are immediately followed by a three-stage decomposition of the anhydrous oxalate to give the end product. The various stages are discussed in detail below.

Dehydration

As seen from the TG curve (Fig. 2), BMO is stable up to 115°C and then loses its water in two stages which may correspond to two moles of water per mole of BMO lost in each stage. The first stage appears to extend up to

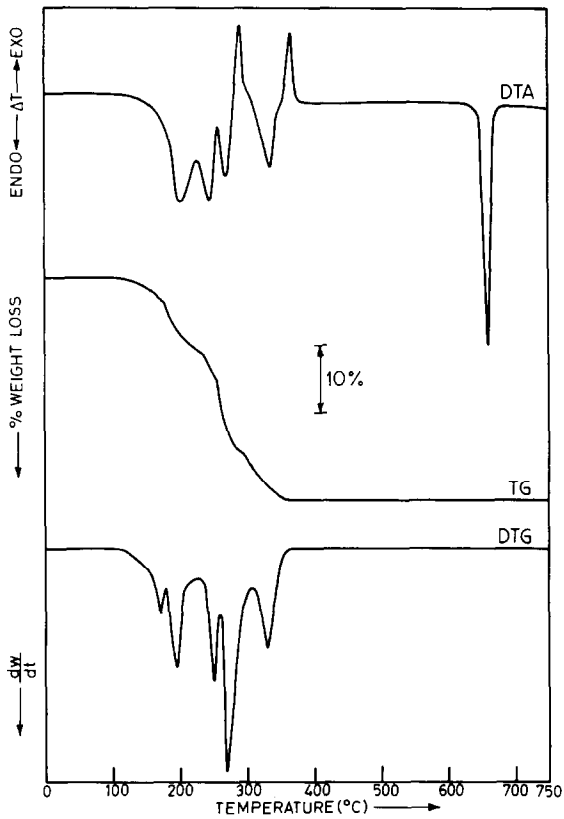

Fig. 2. DTA, TG and DTG of BMO in air.

175°C while the second appears to occur between 175 and 230°C. The observed weight loss for these stages is 3.84 and 7.14%, respectively, while the calculated values for two moles of water being lost in each stage is 5.47 and 5.48%, respectively. It appears that the second stage starts long before the completion of the first. The two stages are observed in DTG as peaks at 170 and 195°C, respectively. However, in DTA only one endothermic peak at about 200°C is observed which may be attributed to the difference in the heating rates during the TG and DTA studies.

Decomposition of oxalate

The decomposition of anhydrous BMO is immediately followed by dehydration, which takes place in three stages. The first stage extends up to 255°C and corresponds to the loss of one mole of carbon monoxide per mole of anhydrous BMO to give an intermediate having the tentative composition $Ba[Mo_2O_5(C_2O_4)(CO_3)]$. The observed weight loss is 4.29% against the calculated value of 4.26%. This is observed in DTA and DTG as peaks at 245 and 250°C, respectively. The second stage occurs between 255 and 295°C and involves a further loss of one mole each of carbon monoxide and carbon dioxide to give another intermediate with the tentative composition $BaMo_2O_7 \cdot CO_2$. The observed weight loss is 10.99% while the calculated value is 10.96%, both DTA and DTG showing peaks at 270°C. However, in DTA the endothermic peak at 270°C is immediately followed by an exotherm at 290°C which may be due to the domination of oxidation of carbon monoxide into carbon dioxide. The third stage occurs between 295 and 360°C and involves a further loss of one mole of carbon dioxide to give the end product. The observed weight loss is 6.70% against the calculated value of 6.69%. This is observed in DTA and DTG as peaks at 335 and 330°C, respectively. The compositions assigned to the intermediates are well supported by the IR spectrum of samples obtained by heating BMO isothermally at 255 (Fig. 1B) and at 295°C (Fig. 1C), the former indicating the presence of both oxalate and carbonate while the latter only indicates the presence of carbon dioxide adsorbed on the solid.

DTA shows an additional exothermic peak at 365°C corresponding to which no weight change is observed on the TG curve. This may be due to the oxidation of some lower or nonstoichiometric oxide formed during the primary decomposition process. Such a reduction of the metal ion has also been observed during the decomposition of other oxalato compounds [14–16].

Melting

DTA also shows an additional endothermic peak at 660°C which, also, does not correspond to any weight change on the TG curve. This peak has been attributed to the melting of the end product, as BMO on heating

isothermally at 665 ± 5°C gives a molten product which immediately solidifies on cooling. Moreover, a survey of the literature also reveals that $BaMo_2O_7$ melts incongruently at 653 ± 3°C [17].

The end product was obtained by heating BMO isothermally at 370 and at 670°C. Both these samples gave identical chemical analyses, IR spectra (Fig. 1D) and X-ray diffraction patterns. In addition to the X-ray diffraction peaks reported for $BaMoO_4$ [18] and $BaMo_2O_7$ [17], the observed X-ray diffraction pattern also has some other peaks which could not be assigned to any simple oxide of barium and molybdenum reported in the literature. The diffractogram also excludes the possibility of the presence of any mixed oxide of barium and molybdenum so far reported in the literature, for example $BaMo_3O_{10}$, $BaMo_4O_{13}$ [19], and Ba_3MoO_6 [20]. This leaves us with the only conclusion that these additional peaks are probably due to the formation of some new phase, say P, which, however, could not be identified. Table 1 also gives the interplanar spacings for P.

All these studies allow us to write the thermal decomposition of BMO as follows.

$$Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2]\cdot 2H_2O \xrightarrow{115->175^\circ C} Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2] + 2H_2O \quad (1)$$

$$Ba[Mo_2O_5(C_2O_4)_2(H_2O)_2] \xrightarrow{175-230^\circ C} Ba[Mo_2O_5(C_2O_4)_2] + 2H_2O \quad (2)$$

$$Ba[Mo_2O_5(C_2O_4)_2] \xrightarrow{230-255^\circ C} Ba[Mo_2O_5(C_2O_4)(CO_3)] + CO \quad (3)$$

$$Ba[Mo_2O_5(C_2O_4)(CO_3)] \xrightarrow{255-295^\circ C} BaMo_2O_7\cdot CO_2 + CO + CO_2 \quad (4)$$

$$n BaMo_2O_7\cdot CO_2 \xrightarrow{295-360^\circ C} x BaMoO_4 + y BaMo_2O_7 + z P + n CO_2 \quad (5)$$

The mechanism proposed here is a tentative one based on the results obtained from dynamic thermogravimetry and isothermal studies. The values of n, x, y and z will depend upon the composition of phase P.

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